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(71) Applicant: **Bayer Corporation**
Pittsburgh, PA 15219-2502 (US)

(72) Inventors:
- **Chung, James Y.J.**
  Wexford, PA 15090 (US)
- **Mason, James P.**
  McKees Rocks, PA 15136 (US)
- **White, Roger J.**
  Washington, PA 15301 (US)
- **DiBernardo, James A.**
  North Braddock, PA 15104 (US)

(74) Representative: **Klimiuk-Japadita, Meike**
Bayer AG,
Konzernzentrale RP,
Patente Konzern
51368 Leverkusen (DE)

(54) Impact modified thermoplastic molding composition containing a silicone rubber powder

(57) The impact strength of a thermoplastic molding composition containing thermoplastic polymers selected from the group comprising aromatic polycarbonate, and thermoplastic (co)polyester, polyamide and copolymer is improved upon the incorporation therewith of a particular silicone rubber powder. The silicone rubber powder, added at a level of about 1 to 25 contains a mixture of (a) a polydiorganosiloxane and (b) finely divided silica filler.

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Description

The invention concerns a thermoplastic molding composition and more particularly a composition containing thermoplastic polymers selected from the group comprising polycarbonate, (co)polyester, polyamide and copolymer.

The invention is based on the surprising and unexpected finding that the impact performance of a thermoplastic composition containing the a.m. thermoplastic polymers is improved upon incorporation therewith of a particular silicone rubber powder. The silicone rubber powder, is characterized in that it contains a mixture of (a) a polydiorganosiloxane and (b) silica.

The thermoplastic polymers are well known and are readily available in commerce. While the impact resistance of polycarbonate makes this resin the material of choice in a variety of demanding applications, attempts at improving this property continue. While the chemical resistance of polyester is well recognized and is the basis for the wide applicability of the resin, its low impact resistance and brittle failure limits the utility of the resin. The art has long recognized and been concerned with improving the impact strength of polyamides. A variety of additives have been suggested and added to polyamides. The literature includes a large number of patents directed to this subject. Thermoplastic polyester resins are also well known and are readily available in commerce. Also known are blends of polycarbonate and thermoplastic polyester.

Of particular relevance in the present context is a paper by R. Buch et al "Silicone-Based Additives for Thermoplastic Resins Providing Improved Impact Strength, Processing and Fire Retardant Synergy". This prior art paper (Dow Corning Corporation) disclosed certain silicone powder resin modifier products termed RM 4-7081 and RM 4-7051 to be useful in reducing the rate of heat release and the evolution rates of smoke and carbon monoxide of burning plastics, including polycarbonate. The relevant properties of compositions containing 99 and 95% polycarbonate, the balance in each composition being RM 4-7081, are reported. Also disclosed is the impact strength improvement for engineering resins such as polyphenylene ether (PPE) and PPS. Improved impact strength of polycarbonate compositions is not reported.

Also related is Canadian Patent Application 2,083,014 which disclosed the silicone rubber powder of the present invention as a component in a composition containing poly(phenylene ether) resin.

Polycarbonate molding compositions which contain additive amounts of organosiloxane compounds are known: JP 5,262,960 is said to disclose a low viscosity polycarbonate resin composition which contains organo siloxane and a catalyst. The composition is said to exhibit lower melt viscosity and improved fluidity and moldability without loss of mechanical properties; JP 5,086,278 is considered to disclose an organosiloxane compound and a catalyst as additives to a polycarbonate resin. EP 505,869 disclosed a polycarbonate composition containing a siloxane compound, characterized in its high dimensional stability. Polycarbonate compositions containing a cyclosiloxane compound were disclosed in U.S. Patent 3,751,519 to have good release properties. A thermal oxidative stabilized polycarbonate composition containing a hydrocarbonoxy siloxane compound has been disclosed in U.S. Patent 4,197,384. U.S. Patent 5,322,882 disclosed a composition having improved impact strength containing a polycarbonate/polyorganosiloxane copolymer.

Many of the additives for polyamides are elastomeric, for instance, U.S. Patent 3,668,274 disclosed improved impact strength by adding a core/shell polymer containing (a) a core made of a cross linked elastomeric phase and (b) a shell made of a rigid thermoplastic phase which contains amine-reactive moieties. An impact resistant polyamide composition containing a graft product of polybutadiene as a graft substrate and a mixture of acrylate and acrylonitrile and or acrylamide monomers grafted thereon was disclosed in U.S. Patent 4,221,879. Also relevant in this context is U.S. Patent 4,167,505; 4,174,358 and 4,584,344.

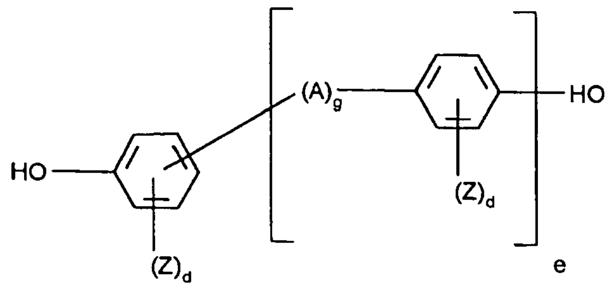
It has now been discovered that certain silicone rubber powders, preferably produced in accordance with the procedure disclosed in U.S. Patent 5,153,238 which is incorporated herein by reference, are useful as impact modifiers in thermoplastic molding compositions containing thermoplastic polymers selected from the group comprising polycarbonate, (co)polyester, e.g. and polyalkylene terephthalate, polyamide and copolymer.

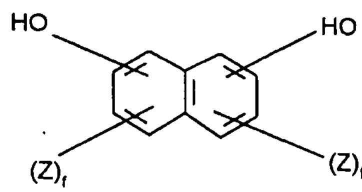
The inventive compositions contain about 1 to 25 percent, preferably 3 to 15 percent relative to the weight of the composition, of the silicone rubber powder.

The polycarbonate resins within the scope of the present invention include (co)polycarbonates and mixtures thereof.

The (co)polycarbonates generally have a weight average molecular weight of 10,000 to 200,000, preferably 20,000 to 80,000 and their melt flow rate, per ASTM D-1238 at 300°C, is about 1 to about 65 g/10 min., preferably about 2 to 15 g/10 min. They may be prepared, for example, by the known diphasic interface process from a carbonic acid derivative such as phosgene and dihydroxy compounds by polycondensation (see German Offenlegungsschriften 2,063,050; 2,063,052; 1,570,703; 2,211,956; 2,211,957 and 2,248,817; French Patent 1,561,518; and the monograph H. Schnell, "Chemistry and Physics of Polycarbonates", Interscience Publishers, New York, New York, 1964, all incorporated herein by reference).

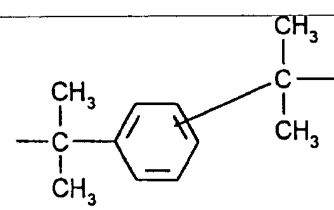
In the present context, dihydroxy compounds suitable for the preparation of the polycarbonates conform to the structural formulae (1) or (2).





wherein

A denotes an alkylene group with 1 to 8 carbon atoms, an alkylidene group with 2 to 8 carbon atoms, a cycloalkylene group with 5 to 15 carbon atoms, a cycloalkylidene group with 5 to 15 carbon atoms, a carbonyl group, an oxygen atom, a sulfur atom, -SO- or $-SO_2-$ or a radical conforming to



e and g both denote the number 0 to 1; Z denotes F, Cl, Br or C_1-C_4-alkyl and if several Z radicals are substituents in one aryl radical, they may be identical or different from one another; d denotes an integer of from 0 to 4; and f denotes an integer of from 0 to 3.

Among the dihydroxy compounds useful in the practice of the invention are hydroquinone, resorcinol, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfoxides, bis-(hydroxyphenyl)-sulfides, bis-(hydroxyphenyl)-sulfones, and α,α-bis-(hydroxyphenyl)-diisopropylbenzenes, as well as their nuclear-alkylated compounds. These and further suitable aromatic dihydroxy compounds are described, for example, in U.S. Patents 3,028,356; 2,999,835; 3,148,172; 2,991,273; 3,271,367; and 2,999,846, all incorporated herein by reference.

Further examples of suitable bisphenols are 2,2-bis-(4-hydroxy-phenyl)-propane (bisphenol A), 2,4-bis-(4-hydroxyphenyl)-2-methyl-butane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, α,α'-bis-(4-hydroxy-phenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfide, bis-(3,5-dimethyl-4-hydroxy-phenyl)-sulfoxide, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, dihydroxybenzophenone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-cyclohexane, α,α'-bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene and 4,4'-sulfonyl diphenol.

Examples of particularly preferred aromatic bisphenols are 2,2,-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

The most preferred bisphenol is 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A). The polycarbonates of the

invention may entail in their structure units derived from one or more of the suitable bisphenols.

Among the resins suitable in the practice of the invention are included phenolphthalein-based polycarbonate, copolycarbonates and terpolycarbonates such as are described in U.S. Patents 3,036,036 and 4,210,741, both incorporated by reference herein.

The polycarbonates of the invention may also be branched by condensing therein small quantities, e.g., 0.05 to 2.0 mol % (relative to the bisphenols) of polyhydroxyl compounds.

Polycarbonates of this type have been described, for example, in German Offenlegungsschriften 1,570,533; 2,116,974 and 2,113,374; British Patents 885,442 and 1,079,821 and U.S. Patent 3,544,514. The following are some examples of polyhydroxyl compounds which may be used for this purpose: phloroglucinol; 4,6-dimethyl-2,4,6-tri-(4-hydroxy-phenyl)-heptane; 1,3,5-tri-(4-hydroxyphenyl)benzene; 1,1,1-tri-(4-hydroxy-phenyl)-ethane; tri-(4-hydroxyphenyl)-phenylmethane; 2,2-bis-[4,4-(4,4'-dihydroxydiphenyl)]-cyclohexyl-propane; 2,4-bis-(4-hydroxy-1-isopropyl-idine)-phenol; 2,6-bis-(2'-dihydroxy-5'-methylbenzyl)-4-methylphenol; 2,4-dihydroxybenzoic acid; 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane and 1,4-bis-(4,4'-dihydroxytriphenylmethyl)-benzene. Some of the other polyfunctional compounds are 2,4-dihydroxybenzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(4-hydroxyphenyl)2-oxo-2,3-dihydroindole

In addition to the polycondensation process mentioned above, other processes for the preparation of the polycarbonates of the invention are polycondensation in a homogeneous phase and transesterification. The suitable processes are disclosed in the incorporated herein by reference, U.S. Patents 3,028,365; 2,999,846; 3,153,008; and 2,991,273.

The preferred process for the preparation of polycarbonates is the interfacial polycondensation process.

Other methods of synthesis in forming the polycarbonates of the invention such as disclosed in U.S. Patent 3,912,688, incorporated herein by reference, may be used.

Suitable polycarbonate resins are available in commerce, for instance, Makrolon FCR, Makrolon 2600, Makrolon 2800 and Makrolon 3100, all of which are bisphenol based homopolycarbonate resins differing in terms of their respective molecular weights and characterized in that their melt flow indices (MFR) per ASTM D-1238 are about 16.5 to 24, 13 to 16, 7.5 to 13.0 and 3.5 to 6.5 g/10 min., respectively. These are products of Bayer Corporation of Pittsburgh, Pennsylvania.

A polycarbonate resin suitable in the practice of the invention is known and its structure and methods of preparation have been disclosed, for example in U.S. Patents 3,030,331; 3,169,121; 3,395,119; 3,729,447; 4,255,556; 4,260,731; 4,369,303 and 4,714,746 all of which are incorporated by reference herein.

The thermoplastic (co)polyester suitable in the present invention comprise repeat units from at least one C_{6-20}-aromatic, C_{3-20}-aliphatic or alicyclic dicarboxylic acid, and repeat units from at least one C_{2-20}- aliphatic glycol.

Examples of the dicarboxylic acids include malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, 1,4-, 1,5- and 2,6-decahydronaphthalene dicarboxylic acid, and cis- or trans-1,4-cyclohexane dicarboxylic acid. Examples of useful aromatic dicarboxylic acid are terephthalic acid; isophthalic acid; trans 3,3'- and trans 4,4'-stilbenedicarboxylic acid, 4,4'-dibenyldicarboxylic acid; 1,4-, 1,5'-, 2,3'-, 2,6, and 2,7-naphthalenedicarboxylic acid. The preferred dicarboxylic acids are terephthalic and isophthalic acid or mixtures thereof.

The preferred glycol of the (co)polyester includes 2 to 8 carbon atoms. Examples include ethylene glycol, 1,2-propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-, 1,3- and 1,4-cyclohexanedimethanol, neopentyl glycol, and 2,2,4,4- tetramethyl-1,3-cyclobutanediol. The preferred diols are 1,4-cyclohexanedimethanol, ethylene glycol, butanediol and mixtures thereof.

The preferred (co)polyesters include resins having repeat units from poly(ethylene terephthalate), poly(butylene terephthalate) or poly(1,4-cyclohexylenedimethylene terephthalate). Preferred (co)polyesters comprise repeat units from terephthalic acid, isophthalic acid or mixtures thereof and 1,4-cyclohexanedimethanol. Other preferred (co)polyesters comprise repeat units from terephthalic acid and 1,4-cyclohexanedimethanol, ethylene glycol or mixtures thereof.

The preparation of the (co)polyesters follow conventional procedures well known in the art such as the process described in U.S. Patent 2,901,466 which disclosure is incorporated herein by reference.

The (co)polyesters of the invention have as a rule inherent viscosity of about 0.4 to 1.0 dl/g, preferably about 0.6 to 0.8 dl/g at 25°C in a solvent containing 60 w/% phenol and 40 w/% tetrachloroethane.

Included among the suitable polyesters are the reaction product of a glycol portion which contains 1,4-cyclohexanedimethanol (CHDM) and ethylene glycol (EG) wherein the molar ratio of CHDM to EG is from about 1:4 to 4:1, with an acid portion comprising at least one of phthalic acid and isophthalic acid. These may be prepared by procedures well known to those skilled in this art, such as by condensation reactions substantially as shown and described in U.S. Patent No. 2,901,466. More particularly, the acid or mixture of acids or alkyl esters of the aromatic dicarboxylic acid or acids, for example, dimethylterephthalate, together with the dihydric alcohols are charged to a flask and heated to temperatures sufficient to cause condensation of the copolymer to begin, for example to 175° to 225°C. Thereafter, the temperature is raised to about 250° to 300°C., and a vacuum is applied and the condensation reaction is allowed to proceed until substantially complete.

The condensation reaction may be facilitated by the use of a catalyst, with the choice of catalyst being d termined

by the nature of the reactants. Th various catalysts for use herein are very well known in the art and are too numerous to mention individually herein. Generally, however, when an alkyl ester of the dicarboxylic acid compound is employed, an ester interchange type of catalyst is preferred, such as NaH $Ti(OC_4H_9)_6$ in n-butanol. If a free acid is being reacted with the free glycols, a catalyst is generally not added until after the preliminary condensation has gotten under way.

The reaction is generally begun in the presence of an excess of glycols and initially involves heating to a temperature sufficient to cause a preliminary condensation followed by the evaporation of excess glycol. The entire reaction is conducted with agitation under an inert atmosphere. The temperature can then be advantageously increased with or without the immediate application of a vacuum. As the temperature is further increased, the pressure can be advantageously greatly reduced and the condensation allowed to proceed until the desired degree of polymerization is achieved. The product can be considered finished at this stage or it can be subjected to further polymerization in the solid phase in accordance with well-known techniques. Thus, the highly monomeric condensation product produced can be cooled, pulverized, and the powder heated to a temperature somewhat less than that employed during the last stage of the molten phase polymerization, thereby avoiding coagulation of the solid particles. The solid phase polymerization is conducted until the desired degree of polymerization is achieved. The solid phase polymerization, among other things, results in a higher degree of polymerization without the accompanying degradation which frequently takes place when continuing the last stage of the melt polymerization at a temperature high enough to achieve the desired degree of polymerization. The solid phase process is advantageously conducted with agitation employing an inert atmosphere at either normal atmospheric pressure or under a greatly reduced pressure.

Among the preferred polyesters of this type suitable for use in the subject invention is a copolyester as described above wherein the glycol portion has a predominance of ethylene glycol over 1,4-cyclohexanedimethanol, for example greater than 50/50 and especially preferably is about 70 molar ethylene glycol to 30 molar 1,4-cyclohexanedimethanol and the acid portion is terephthalic acid.

A commercially available copolyester of this preferred type is EKTAR 6763 PETG sold by the Eastman Kodak Company.

The copolymers of the invention are characterized in that their weight average molecular weight (determined by light scattering or by sedimentation) is about 15,000 to 200,000 made of at least two ethylenically unsaturated monomers. The suitable monomers include vinyl aromatic hydrocarbons, such as styrene and halogen and/or alkyl substituted vinyl aromatics, exemplified by halogen and/or alkyl substituted styrene, acrylonitrile and substituted acrylonitrile, acrylate and alkyl substituted acrylates, methacrylates, alkyl substituted methacrylates and ethylenically unsaturated carboxylic acids, diacids, dianhydrides, acid esters, diacid esters, amides, imides and N-substituted imides.

Preferred monomers include styrene, 3-methylstyrene; 3,5-diethylstyrene and 4-n-propylstyrene, α-methylstyrene, α-methylvinyltoluene, α-chlorostyrene, vinyltoluene, α-bromostyrene, chlorophenylethylenes, dibromophenylethylenes, tetrachlorophenylethylenes, 1-vinylnaphthalene, 2-vinylnaphthalene, acrylonitrile, ethacylonitrile, methacrylonitrile, α-chloroacrylonitrile, β-chloroacrylonitrile, α-bromoacrylonitrile and β-bromoacrylonitrile, methylacrylate, methylmethacrylate, ethylacrylate, butylacrylate, propylacrylate, isopropylacrylate, isobutylacrylate, and mixtures thereof. The preferred monovinyl aromatic hydrocarbon used herein is styrene and/or a-methylstyrene, acrylonitrile, ethylacrylate and methylmethacrylate. In a more preferred embodiment, the copolymer is formed from at least one first monomer selected from the group consisting of styrene, alpha methyl styrene, dibromostyrene and methyl methacrylate and at least one second, different monomer selected from the group consisting of acrylonitrile, methyl methacrylate, malaeic anhydride, maleimide, N-phenyl maleimide and acrylamide. Preferably, the first monomer form about 60 to 95 percent, preferably 50 to 80 percent and the second monomer forms about 5 to 40 percent, preferably 20 to 40 percent relative to the weight of the copolymer. The preferred copolymer is styrene acrylonitrile (SAN).

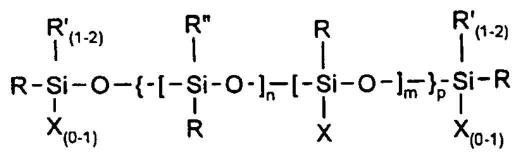
The preparation of suitalbe copolymeric resins by radical polymerization, more especially by emulsion, suspension, solution or bulk polymerization is described in the literature. Suitable copolymers are readily available in commerce, including SAN copolymers which may be obtained from Monsanto under the trademark Lustran.

The polyamide matrix resin which is suitable for the preparation of the toughened composition of the present invention is well known in the art and is readily available in commerce. Embraced within the scope of the term are semi-crystalline and amorphous polymeric resins having a number average molecular weight (determined by end-group analysis) of about 5,000 to 30,000 commonly referred to as nylons. Preferably, the molecular weight is in the range of about 8,000 to 20,000. Suitable polyamides include those described in U.S. Patents 2,071,250; 2,071,251; 2,130,523; 2,130,948; 2,241,322; 2,312,966; 2,513,606; and 3,393,210, the disclosures of which are incorporated herein by reference. Essentially, the polyamide resin can be produced by condensation of equimolar amounts of a saturated dicarboxylic acid containing 4 to 12 carbon atoms with a diamine, in which the diamine contains 4 to 14 carbon atoms. Excess diamine can be employed to provide an excess of amine end groups over carboxyl end groups in the resulting polyamide. Examples of polyamides include polyhexamethylene adipamide (nylon 66), polyhexamethylene azelamide (nylon 69), polyhexamethylene sebacamide (nylon 610), polyhexamethylene dodecanoamide (nylon 612) and bis(paraaminocyclohexyl)methane dodecanoamide. Th polyamide resin can also be produced by ring opening of lactams, for example polycaprolactam and polylauric lactam, and by condensation of ω-amino carboxylic acids, for example, poly-11-aminoundecanoic acid. Copoly-amides prepared by copolymerization of two or more of the above polymers or their com-

ponents, may also be used. The preferred polyamides are nylon 6, nylon 66, and copolymers of nylon 6 and nylon 66. Preferably the polyamides are linear and have a melting temperature in excess of 200°C.

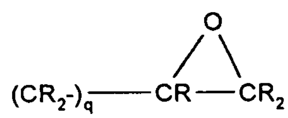
The silicone rubber powder of the invention has an average particle size of about 1 to 1000 microns and contains (i) 100 parts by weight (pbw) of a polydiorganosiloxane and (ii) about 10 to 80 pbw, preferably, about 20 to 50 pbw of a finely divided silica filler.

The polydiorganosiloxane which is characterized in that its viscosity at 25°C is about 10^6 to 10^9 centipoise is a (co)polymeric resin having siloxane structural units represented by the general formula

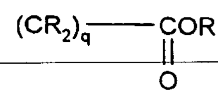


wherein R, R' and R" independently denote hydrogen, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals or aryl groups, and where p is about 1000 to 8000, preferably about 3000 to 6000 and where the relative weight proportions of n and m are 98.5 to 100:0 to 1.5, preferably 99:1, and where

X denotes a member selected from the group consisting of



and



where R denotes hydrogen, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals or aryl groups and where q is 1 to 10.

The organic groups of the polydiorganosiloxane, which may optionally be halogenated, are preferably lower alkyl radicals containing 1 to 4 carbon atoms, phenyl and halogen substituted alkyl radicals. Examples include resins containing dimethylsiloxy units, phenylmethyl-siloxy units and dimethylsiloxy units and diphenyl siloxy units. Most preferably, the polydiorganosiloxane contains vinyl group(s) or epoxy group(s) at its chain termination(s) and/or along its main chain. The methods for the preparation of suitable polydiorganosiloxane are well known; a typical method comprises the acid- or base-catalyzed polymerization of cyclic diorganosiloxanes.

The silica filler required in the silicone rubber powder is a finely divided silica selected from among fumed silica and precipitated silica or silica gel. These are well known forms of silica and are readily available in commerce. The suitable silica is characterized in that its surface area is at least 50 m^2/g, preferably 50 to 900 m^2/g.

An additional embodiment entails use of treated silica which contains sites bonded to groups X as defined above; the manufacture of treated silica, typically by reacting the silanol groups on the silica surface with about 1 to 2% by weight of an organic alkyl halide compound or an organosilicon halide compound, is known in the art.

Among the suitable compounds, mention may be made of low molecular weight liquid hydroxy-or alkoxy-terminated polydiorgano-siloxanes, hexaorganosiloxanes and hexaorganosilazanes.

The procedure for the preparation of the silicone rubber powder has been described in detail in U.S. Patent 5,153,238, the specification of which is incorporated herein by reference. Suitable silicone rubber powder is available in commerce from Dow Corning Corporation under the trademark RM 4-7051 and RM 4-7081.

The following compositions are particularly preferred:

1. An aromatic polycarbonate resin containing the silicone rubber powder added at a level of greater than 1 and less than 5, preferably 2 to less than 4,5% by weight, relative to the weight of the composition.

2. A thermoplastic (co)polyester containing 8 to 25, especially 10 to 20% by weight, relative to th weight of the composition of the silicone rubber powder.

3. A composition of aromatic polycarbonate and the a.m. copolymer containing 3 to 25, especially 5 to 20 parts by weight of the silicone rubber powder.

The amount of aromatic polycarbonate in the composition is preferably 40 to 95 especially 50 to 90 parts by weight and the amount of the copolymer is preferably 5 to 50, especially 10 to 40 parts by weight.

4. A composition of aromatic polycarbonate and (co)polyester containing 3 to 25, especially 4 to 15 parts by weight of the silicone rubber powder.

The amount of aromatic polycarbonate in the composition is preferably 40 to 95 especially 60 to 85 parts by weight, the amount of the (co)polyester is preferably 5 to 60, especially 15 to 40 parts by weight.

5. A polyamide composition containing 1 to 25, especially 3 to 15% by weight, relative to the weight of the composition of the silicone rubber powder.

The preparation of the composition of the invention is carried out following conventional procedures and by use of conventional means such as single, preferably twin screw extruders. Conventional thermoplastic processes are suitable in molding useful articles from the inventive composition.

Conventional additives may be incorporated in the composition of the invention in the usual quantities. Mention may be made of a thermal stabilizer, a mold release agent, a pigment, a flame retarding agent, a uv stabilizer, a hydrolysis stabilizer, a gamma radiation stabilizer and a plasticizer for polycarbonate compositions, as well as fillers and reinforcing agents such as glass fibers.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

Examples:

Compositions in accordance with the invention have been prepared following well-known procedures and their properties determined as described below:

In Examples 1-3, the polycarbonate resin was Makrolon 3100 resin, a Bayer product (a bisphenol-A based homopolycarbonate having a MFR of about 6 g/10 min. in accordance with ASTM D-1238 (@ 300°C under 1200 g load); the silicone rubber powder was Dow Corning's RM 4-7051. The thermoplastic polyester was Ektar 12822 from Eastman, a polyethylene terephthalate having inherent viscosity of 0.9 dl/g. Composition 2 contained brominated PC oligomer (8.5%), brominated phosphate 3%, bisbenzotriazole 1.5% and PTFE 1%, having no criticality to the improved impact strength of the inventive composition. The notched Izod impact strength was measured at 73°C.

Table 1

Example	1	2	3
Thermoplastic polyester, wt. %	30	30	33
Polycarbonate, wt. %	62	48	67
Silicone rubber powder wt. %	8	8	0
Impact Strength, notched Izod,ft.lb/in 1/8"	17.6	10.7	2
Impact Strength, notched Izod,ft lb/in 1/4"	14.5	4	2
Failure mode	ductile	ductile	brittle
Flammability rating UL-94,1/16"	fail	V-0	N/A
Delamination[1]	none	none	none

[1] by visual assessment

In an additional set of examples, the evaluation of which are summarized in Table 2 below, the resinous components of the compositions were the same as in Examples 1-3 above.

Table 2

Example	4	5	6	7
Thermoplastic Polyester, wt. %	68	68	62	60
Polycarbonate, wt %	32	29	28	25
Silicone rubber powder, wt. %.	0	3	10	15
Impact strength, notched Izod ft.lb./in.1/8"	1.0	1.3	15.4	14.5
Impact strength, notched Izod ft.lb./in.1/4"	0.8	1.4	3.8	7.7

The data presented above show the beneficial effect on the impact strength, the basis of the inventive finding, in compositions which are polyester-rich. It would be noted that no delamination was observed in the compositions of the invention. Additional data summarizing the results of the evaluation of compositions of the inventions where the resinous components are polycarbonate-rich, are presented in Table 3.

Table 3

Example	8	9	10	11
Thermoplastic Polyester, wt. %	33	29	30	25
Polycarbonate, wt %	67	68	62	60
Silicone rubber powder, wt. %.	0	3	8	15
Impact strength, notched Izod ft.lb./in.1/8"	2.3	2.7	17.6	14.2
Impact strength, notched Izod ft.lb./in.1/4"	ND[a]	2.2	14.5	7.7

[a] not determined

In examples 12-14, the polycarbonate resin was Makrolon 3100 resin, a Bayer product (a bisphenol-A based homopolycarbonate having a MFR of about 6 g/10 min. in accordance with ASTM D-1238 @ 300 C under 1200 g load); the silicone rubber powder was Dow Corning's RM 4-7051. Compositions 12 and 14 show the advantageous impact strength (notched Izod, ¼") in compositions having low MFR values.

Table 4

Example	12	13	14
Polycarbonate, wt.%	100	99	95.1
Silicone rubber powder wt. %	0	1	4.9
MFR, g/10 min.	5.65	5.53	5.5
Flexural strength, Kpsi	12.6	12.4	12.0
Flexural modulus, psi x 10^5	3.50	3.44	3.35
HDT, C			
at 66 psi	140.2	138.5	138.5
at 264 psi	127.7	128	126.3
Impact strength ft. lb./in. Izod notched			
1/8"	19.3	18	17.6
1/4"	2.2	3.1	16.4
Flammability rating UL-94	V-2	V-2	V-2

In an additional set of examples, compositions 15-18, the polycarbonate component had a high MFR, of about 40.8g/10 min. Each of these compositions contained a conventional release agent and pigment (totaling about 1.4% of the composition) the chemical nature of which having no critically to the invention.

Table 5

Example	15	16	17	18
Polycarbonate, wt.%	98.6	95.5	93.6	91.8
Silicone rubber powder, wt.%	0	3.1	5.0	6.9
MFR, g/10 min.	40.8	39.2	34.1	34
Impact strength, ft. lb./in				
Izod, notched				
1/8"	2.2	11	8.7	7.5

[1] average values

The data presented in tables 4 and 5 show that the beneficial effect on the impact strength, the basis of the inventive finding, is maximized at less than 5% addition of the silicone rubber powder.

In the examples 19 to 23 the thermoplastic polyester resin was polyethylene terephthalate having an inherent viscosity of about 0.9 dl/g Ektar 12822 a product of Eastman); the silicone rubber powder was Dow Corning's RM 4-7051. The advantageous impact strength (notched Izod, 1/8") is apparent.

Table 6

Example	19	20	21	22	23
PE, wt%	100	97	90	85	80
Silicone rubber powder, wt.%	0	3	10	15	20
Impact strength notched Izod, 1/8" ft.lb/in.	0.5	0.7	1.4	9.1	10.2

The compositions according to examples 24 to 26 have been prepared following well-known procedures and their properties determined as described below: the polyamide resin was nylon 6, available from Bayer Corporation as Durethan B40K resin; the silicone rubber powder was Dow Corning's RM 4-7051. Compositions 20 and 21 show the advantageous impact strength (notched Izod, 1/8").

All the compositions were produced by extruding in a twin screw extruder and injection molded (3 oz. Newbury).

Since the impact strength of polyamide is highly dependent on its moisture content, the impact strength was determined on specimens as molded and on conditioned samples. The impact strength of the as molded specimens was determined 24 hours after molding; during the 24 hours period, the specimens were held at 50% relative humidity at 73°F. The notched Izod impact strength of the conditioned specimens was determined 14 days after molding. During the 14 days period the specimens were first immersed in deionized water for seven days at 73°F and then removed from the water and sealed in an air tight bag for seven days at 73°F. The impact strength and moisture absorption of the samples were determined using ASTM D256 and D570 respectively.

A summary of the results is presented below. Instrumented impact measured as total energy, dart impact, speed of the dart 15 miles per hour, was determined in accordance with ASTM D 3763. The unnotched values of the composition showed no advantage for using the silicon rubber powder.

Table 7

Example	24	25	26
Polyamide, wt. %	100	97	90
Silicone rubber powder wt. %	0	3	10
Water Absorption, as molded	1	1	1
Water absorption, conditioned	9	9	9
Dart Impact, ft.lb at 73 F	8.4	2.7	2.7
Impact strength, ft. lb./in. notched Izod 1/8"			
as molded	1	1.4	2.5
conditioned	1.9	3.2	13.7

In Examples 27 through 32, the polycarbonate resin was Makrolon 2600 resin, a Bayer product (a bisphenol-A based homopolycarbonate having a MFR of about 11 g/10 min. in accordance with ASTM D-1238 @ 300°C under 1200 g load; in composition 33 and 34, the polycarbonate was Makrolon 6030, a copolycarbonate of brominated bisphenol-A, having a MFR of about 4 g/10 min. and containing about 5.5% of bromine. In all the examples, the copolymer was Lustran SAN33, a product of Monsanto (72% styrene and 28% acrylonitrile). The silicone rubber powder was Dow Corning's RM 4-7051.

Table 8

Example	27	28	29	30	31	32
polycarbonate, wt%	65	62	60	80	73.6	68
SAN, wt%	35	35	32	20	18.4	17
Silicone rubber powder, wt%	0	3	8	0	8	15
Impact strength, Notched Izod 1/8" ft.lb/inch	0.3	1.0	1.0	1.3	4.6	5.6

In Examples 33 and 34, the polycarbonate resin used was a copolycarbonate of BPA and bromine-substituted BPA. Both compositions contained as a flame retarding package, triphenyl phosphate and PTFE, neither of which are critical to the invention. The SAN and silicone rubber powder were as noted above.

Table 9

Example	33	34
Copolycarbonate, wt%	79.2	72.1
SAN, wt%	13.8	12.5
Silicone rubber Powder, wt %	0	8.9
Impact strength, Notched Izod 1/8" ft.lb/inch	0.4	9.0

The finding giving rise to the invention were supplemented by Example 35 where a SAN-rich composition (55% SAN, 30% polycarbonate and 15% silicon rubber powder) show no advantages in terms of impact strength.

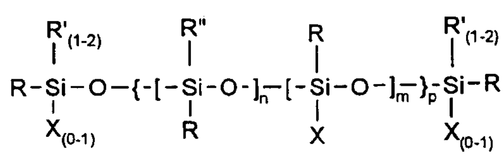
Claims

1. A thermoplastic molding composition comprising

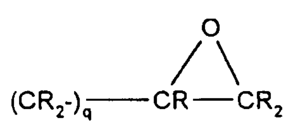
A) a thermoplastic polymer selected from the group comprising polycarbonate, (co)polyester, polyamide and copolymer of at least two ethylenically unsaturated monomers or mixtures thereof and

B) a silicone rubber powder,
wherein said powder is present in the composition in an amount of 1 to 25% by weight, relative to the weight of the composition, said silicone rubber powder having an average particle size of 1 to 100 microns and containing

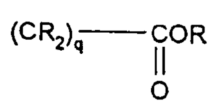
(i) 100 pbw of a polydiorganosiloxane having a viscosity at 25°C is about 10^6 to 10^9 centipoise and siloxane structural units represented by the general formula



wherein R, R' and R" independently denote a hydrogen atom, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals or aryl groups, and where p is about 1000 to 8000 and where the relative weight proportions of n and m is 98.5 to 100:0 to 1.5, and where
X denotes a member selected from the group consisting of



and



where R denotes hydrogen, C_{1-10}-alkyl, alkenyl, cycloalkyl radicals or aryl groups and where q is 1 to 10,

and

(ii) about 10 to 80 pbw of a finely divided silica selected from among fumed silica, precipitated silica and silica gel having a surface area of at least 50 m^2/g.

2. The composition of Claim 1 wherein said hydrocarbon radical is selected from the group consisting of C_{1-10}-alkyl radicals; alkenyl radicals; cycloalkyl radicals; and aromatic hydrocarbon radicals.

3. The composition of Claim 2 wherein said hydrocarbon radical is a lower alkyl radical containing 1 to 4 carbon atoms or a phenyl radical.

4. The composition of Claim 1 wherein said silica has a surface area of about 50 to 900 m^2/g.

5. The composition of Claim 1 wherein said p is about 5000 to 6000.

6. The composition of Claim 1 wherein the relative weight proportions of n and m is 99:1.

7. The composition of Claim 1 wherein said silica contains sites bonded to said X.

8. The composition of Claim 1 further containing at least one member selected from the group consisting of a thermal stabilizer, a mold release agent, a pigment, a flame retarding agent, a uv stabilizer, a hydrolysis stabilizer, a gamma radiation stabilizer, a plasticizer, a filler and a reinforcing agent.

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(71) Applicant: Bayer Corporation
Pittsburgh, PA 15205-9741 (US)

(72) Inventors:
- Chung, James Y.J.
  Wexford, PA 15090 (US)
- Mason, James P.
  McKees Rocks, PA 15136 (US)
- White, Roger J.
  Washington, PA 15301 (US)
- DiBernardo, James A.
  North Braddock, PA 15104 (US)

(74) Representative:
Klimiuk-Japadita, Meike
Bayer AG,
Konzernbereich RP
Patente und Lizenzen
51368 Leverkusen (DE)

(54) Impact modified thermoplastic molding composition containing a silicone rubber powder

(57) The impact strength of a thermoplastic molding composition containing thermoplastic polymers selected from the group comprising aromatic polycarbonate, and thermoplastic (co)polyester, polyamide and copolymer is improved upon the incorporation therewith of a particular silicone rubber powder. The silicone rubber powder, added at a level of about 1 to 25 contains a mixture of (a) a polydiorganosiloxane and (b) finely divided silica filler.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 11 0192

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 391 594 A (ROMENESKO, DAVID J. ET AL) 21 February 1995 * claims 1-7 * * column 4, line 50 - column 7, line 7 * * column 12, line 55 - column 14, line 17 *	1-4,8	C08L69/00 C08L67/02 C08L77/00 C08L101/00 C08L83/04 //(C08L69/00, 83:04), (C08L67/02, 83:04), (C08L77/00, 83:04), (C08L101/00, 83:04), (C08L69/00, 67:02,83:04), (C08L67/02, 69:00,83:04), (C08L69/00,
A D	EP 0 543 597 A (DOW CORNING) 26 May 1993 * abstract; claim 1 * * page 3, line 35 - page 4, line 44 * & CA 2 083 014 A	1-4,8	
D,A	EP 0 505 869 A (BAYER AG) 30 September 1992 * claims 1,2 * * page 4, line 14 - line 34 *	1,6	
A	DATABASE WPI Section Ch, Week 7604 Derwent Publications Ltd., London, GB; Class A23, AN 76-06262X XP002080678 ~~& JP 50 096650 A (UNITIKA LTD)~~ , 31 July 1975 * abstract *	1-3,8	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08L C08K C08J
A	EP 0 596 734 A (JAPAN SYNTHETIC RUBBER CO LTD; NTN CORP.) 11 May 1994 * claims 1,8,11; example 7 * * page 5, line 35 - line 55 *	1-3,8	
A	US T941003 I (T.G. DAVIS ET AL.) 2 December 1975 * the whole document *	1	
A	DE 33 14 355 A (PETRARCH SYSTEMS INC) 27 October 1983 * claims 1-3; examples 1,2,6 *	1-3	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	15 October 1998	Krische, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 96 11 0192

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO 86 03213 A (STAMICARBON) 5 June 1986 * claim 1; examples 1,9 * * page 5, line 19 - line 28 *	1-3,8	25:12,83:04)
X	BE 622 377 A (TEXAN-U.S. CHEMICAL COMP.) * claim; table II *	1-3	
A	EP 0 006 521 A (BAYER AG) 9 January 1980 * claim *	1-3,8	
A	EP 0 260 004 A (MOBIL OIL CORP) 16 March 1988 * abstract; example 1 *	1-3	
P,A	DATABASE WPI Section Ch, Week 9627 Derwent Publications Ltd., London, GB; Class A26, AN 96-263855 XP002080679 & JP 08 109262 A (DOW CORNING TORAY SILICONE), 30 April 1996 * abstract *	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP 0 541 988 A (DOW CORNING TORAY SILICONE) 19 May 1993 * abstract * * page 5, line 29 - line 36 *	1-3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	15 October 1998	Krische, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 96 11 0192

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-8

   molding composition containing polycarbonate and silicone rubber powder

2. Claims: 1-8

   molding composition containing (co)polyester and silicone rubber powder

3. Claims: 1-8

   molding composition containing polyamide and silicone rubber powder

4. Claims: 1-8

   molding composition containing vinylaromatic (styrene) copolymers and silicone rubber powder

5. Claims: 1-8

   molding composition containing copolymers of at least two ethylenically unsaturated monomers other then vinylaromatics and silicone rubber powder